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(54) Membrane having a porous surface

(57) A membrane in the form of a flat film, tubular film or hollow filament of synthetic polymers which has from 10 to 90%, by volume, of intercommunicating pores and a smooth surface comprising open pores, the proportion of openings in the surface amounting to from 10 to 90%, is produced by a process which comprises extruding a homogeneous mixture of at least two components, one component being a fusible polymer and another component being a liquid inert to the polymer and both components forming a binary system which, in liquid aggregate state, has a region of complete miscibility and a region with miscibility gaps, at a temperature above the dissociation temperature into a bath which contains the

inert liquid of the extruded component mixture and which has a temperature and hardening the membrane formed in the form of a flat film, tubular film or hollow filament.

GB 2 026 381 A

SPECIFICATION

Membrane having a porous surface

5 This invention relates to a membrane having a porous surface; more particularly, it relates to a membrane in the form of a flat film, tubular film or hollow filament of synthetic polymers, to a process for the production thereof and to the use thereof, particularly as a filter or membrane support for separation purposes.

10 Membranes in the form of flat films, tubular films or hollow filaments have been known for some time. Several processes are available for producing such membranes from a variety of different polymers. Hollow filaments may be used in the manufacture of textile products. However, they are also used, for example, for filtration, ultrafiltration, microfiltration, dialysis and reverse osmosis.

20 Where membranes in the form of flat films, tubular films or hollow filaments are used in separation units, the permeability and selectivity of the membranes are critical factors because the membranes are intended on the one hand to retain certain substances and, on the other hand, to allow other substances, for example the solvent of a solution, to pass through as quickly as possible.

30 Films having a microporous or porous structure have been known for some time. Thus, German Offenlegungsschrift No. 2,737,745, *inter alia*, describes processes for the production of films having a porous or microporous structure. The structures described therein are undoubtedly valuable products which are used for a number of applications.

40 However, it has been found by following the teaching contained therein that the films in question generally have a closed surface. In particular, it is not possible to obtain films which, on both sides, have pores that are directly visible at the surface in the form of openings. Accordingly, there is still a need for improved production techniques and, in particular, for processes which lead to films which combines high permeability with high selectivity and which, in addition, have open pores on both surfaces and, at the same time, a smooth, even surface structure.

50 A process for the production of permeability-selective hollow fibres is described, for example, in German Auslegeschrift No. 1,494,579 in which an intimate mixture of a thermoplastic polymer with a plasticiser is melt-spun and the plasticiser is subsequently extracted from the hollow fibres obtained. In this process, it is necessary, *inter alia*, to be able to remove the plasticiser easily and substantially completely from the spun hollow fibres. However, this frequently requires a relatively long treatment of the filament during the extraction stage. Nor is it always possible completely to remove the plasticiser. 65 In addition, the hollow fibres produced by this

process have a relatively low permeability. Furthermore, it is not possible to vary the proportions of plasticiser and polymer over wide ranges. If a high proportion of plasticiser is used, filament formation no longer occurs while, if the plasticiser content is too low, inadequate permeability is obtained. In addition, the plasticiser is in danger of being inadequately distributed in the thermoplastic polymer during mixing, resulting in agglomerations which, during washing out, lead to holes or overlarge pores which prevent the hollow fibres from being used for numerous purposes.

80 German Auslegeschrift No. 2,346,011 describes another process for the production of hollow filaments in which a solution of a copolymer of acrylonitrile is spun into an aqueous solution of mineral salts. In this process, coagulation liquid also has to be injected into the interior for internal coagulation. The process described therein is relatively complicated. In addition, it is difficult to obtain hollow filaments having uniform properties.

90 U.S. Patent No. 3,674,628 describes a process in which a solution of a fibre-forming polymer is initially spun, after which the outer zone and, optionally, also the inner zone are subjected to gel formation, followed or accompanied by coagulation of both zones. This results in the formation of a hollow fibre which has a skin-like structure both internally and also externally. This process is also relatively complicated, in addition to which the permeability of the hollow filaments obtained is unsatisfactory.

100 Although numerous membranes in the form of flat films, tubular films or hollow filaments are known, there is still a need for improved membranes, particularly for membranes which may be easily produced from a simple spinning melt without any need for complicated spinning baths. In addition, there is need for improved membranes which are porous and 110 which are distinguished, *inter alia*, by high permeability coupled with high selectivity.

An object of the present invention is to provide porous membranes which are distinguished from known membranes by a favourable open surface and in which both the outer wall and also the inner wall have a structure which, although provided with open pores, is nevertheless smooth. Another object of the present invention is to provide membranes 120 which may be used in the textile field, in the technical field and also in the medical field, for example in separation processes, and which are particularly suitable for use as filters, microfilters, membrane supports and as supporting substances for certain substances.

This object is achieved by membranes in the form of flat films, tubular films or hollow filaments of synthetic polymers which are characterised in that they contain from 10 to 130 90%, by volume, of inter-communicating

pores and have a smooth surface comprising open pores, the proportion of open pores in the surface amounting to from 10 to 90%. The apparent density of the hollow filaments amounts to from 10 to 90% of the true density of the polymer used; the permeability coefficient of the hollow filaments amounts to at least $10 \times 10^{-12} \text{cm}^2$.

The membranes may be used as filters and, in particular, as filters for microfiltration.

The membranes may also be used as membrane supports, i.e. there is applied to the membrane a layer which also acts as a membrane, optionally having different permeabilities and different selectivities.

The membranes may also be used as supporting substrates, i.e. the membranes may be impregnated with certain substances which are intended to be released at a later stage.

They may also be used as oxygenators.

Accordingly, a further object of the present invention is to provide a process in which polymers may readily be transformed into an extrudable spinning composition and which, at the same time, enables this spinning composition to be extruded and hardened without any need for complicated spinning techniques or spinning baths. Another object of the present invention is to provide a process which enables membranes having an adjustable porosity or permeability to be obtained simply by varying the process parameters.

This object is achieved by a process for the production of porous hollow filaments which is characterised in that a homogeneous mixture of at least two components, one component being a fusible polymer and the other component a liquid inert to the polymer and both components forming a binary system which, in the liquid aggregate state, has a region of complete miscibility and a region with miscibility gaps, is extruded at a temperature above the dissociation temperature into a bath which contains the inert liquid of the extruded component mixture and which has a temperature below the dissociation temperature, followed by hardening of the membrane formed in the form of a flat film, tubular film or hollow filament.

After hardening, the membrane structure formed may be washed out with a solvent, acetone being particularly suitable for this purpose.

It is advantageous to maintain an air gap between the exit surface of the extrusion die and the surface of the bath. The air gap may be heated.

It is also possible directly to extrude the homogeneous mixture into the bath.

One particular embodiment of the present process is characterised in that a temperature-graduated bath is used. The bath may consist of one or more parts which have a temperature gradient such that the temperature continuously decreases from the beginning of the

spinning bath to its outlet end.

It is also possible to use two or more separate baths each having a different temperature.

It has been found to be favourable for the bath to have a temperature which is lower by at least 100°C than the dissociation temperature of the binary composition used. It is also possible, particularly in the case of tubular films and hollow filaments, initially to extrude the homogeneous mixture into a spinning tube preceding the bath and filled with the bath liquid.

According to the present invention, it is possible to extrude homogeneous mixtures of from 10 to 90%, by weight, of polymer and from 90 to 10%, by weight, of inert liquid.

Polypropylene is preferably used as the polymer whilst N,N-bis-(2-hydroxy ethyl)-hexadecyl amine is preferably used as the inert liquid.

The two components, i.e. the molten polymer and the inert liquid, are best continuously mixed before extrusion. In this respect, it is favourable to carry out mixing immediately before extrusion. The mixture may also be homogenised before extrusion. A pinned-disc mixer is particularly suitable for mixing.

For carrying out the present process and for producing the membranes according to the present invention, it is possible to use conventional substances, particularly fibre-forming macromolecular substances, above all synthetic polymers of the type obtained, for example, by polymerisation, polyaddition or polycondensation. The polymer must be fusible, i.e. must be able to change into the liquid aggregate state without decomposing, and must form with a liquid inert to it a binary system which, in the liquid aggregate state, has a region of complete miscibility and a region with miscibility gaps.

In the liquid state, such systems have a phase diagram of the type reproduced, for example, for the aniline-hexane system on page 724 of S. Glasstone's Text Book of Physical Chemistry, Macmillan and Co. Ltd., St. Martin's Street, London, 1953. In this diagram, complete miscibility is indicated for the two components above the curved curve. Below the curve, two liquid phases are in equilibrium with one another.

It is not absolutely essential to the practicability of the present invention for each of the two components to show considerable solubility in relation to the other component in the two-phase region, as is the case in the above-mentioned diagram. In many cases, it is sufficient for marginal solubility to exist in the liquid two-phase region. However, it is essential for the two components to form two liquid phases alongside one another in the liquid state. To this extent the systems which may be used in accordance with the present invention differ from those systems in which, when

the temperature is reduced, the dissolved polymer directly precipitates in the form of a solid without first passing through the liquid aggregate state during cooling.

- 5 According to the present invention, it is possible to use conventional fusible polymers, such as the polymers polyethylene, polypropylene, polyvinyl chloride, polyacrylates and polycaprolactam obtained by polymerisation and
10 corresponding copolymers; polycondensation polymers, such as polyethylene terephthalate, polybutylene terephthalate, polyamide-6,6 and polyphenylene oxide, and also polyaddition polymers, such as polyurethanes and polyureas.

- 15 According to the present invention, the inert liquid used may in principle be any liquid which forms a binary system of the above-mentioned type with the polymer in the liquid
20 state. The expression "inert to the polymer" means that the liquid does not cause any significant degradation of the polymer or does not react with the polymer itself over a short period.

- 25 Although the above-mentioned phase diagram of the aniline-hexane system reproduces the conditions for a binary mixture which, basically, only consists of two substantially pure, uniform substances, the expression "binary systems" is not intended according to
30 the present invention to be strictly applied to mixtures of only two pure, uniform substances. Those skilled in the art know that a polymer is made up of a number of molecules of different molecular weight, so that it is
35 possible in the context of the present invention to regard such polymers having a corresponding molecularweight distribution as a component; the same also applied to copolymers. Under certain conditions, even polymer mixtures may behave like a uniform
40 component, may form a single-phase mixture with the inert solvent and may separate into two liquid phases below the critical temperature. However, it is preferred to use only one polymer.

- 45 Neither does the liquid necessarily have to be completely pure and represent a complete uniform substance. Thus, even relatively small quantities of impurities and possibly even fractions of homologous compounds, of the type
50 formed during production on a large scale, may be present in many cases.

- To carry out the present process, a homogeneous mixture is prepared from the two components at the necessary temperatures. This may be done by mixing the inert liquid with the size-reduced polymer and heating the resulting mixture to corresponding temperatures, provision being made for adequate mixing.
60

- In another suitable process, the two components are separately heated to the requisite temperature and are continuously mixed with
65 one another in the required quantitative ratio

shortly before extrusion. Mixing may be carried out in a pinned-disc mixer which is best arranged between the metering pumps for the individual components and the spinning

- 70 pump. Subsequently homogenisation may be advisable.

In many cases, it is advisable to deaerate the homogeneous mixture before extrusion by applying a suitable vacuum.

- 75 The ratio of polymer to inert liquid in the spinning composition may be varied within wide limits. By adjusting the ratio of polymer to inert liquid, it is possible to a large extent to control the pore volume in the interior and
80 also the surface structure, such as the number of open pores on the surfaces of the membrane obtained. In this way, it is possible to obtain membranes suitable for a variety of different applications.

- 85 In general, it is sufficient for the temperature of the homogeneous mixture before extrusion to be only a few degrees above the critical temperature or above the dissociation temperature according to the particular composition.
90

- However, it is also possible to obtain interesting effects in regard to the structure of the membrane obtained by increasing the difference between the temperature of the homogeneous mixture to be extruded and the dissociation temperature.
95

- The homogeneous spinning composition is then extruded into a bath which contains the inert liquid of the extruded component mixture and which has a temperature below the dissociation temperature. The bath preferably consists completely or largely of the inert liquid which is also present in the extruded mixture. The temperature of the bath lies
100 below the dissociation temperature of the binary mixture used, i.e., below the temperature above which the two components are miscible completely homogeneously with one another. The temperature of the bath is preferably at
105 least 100°C below the dissociation temperature of the mixture used.

- The temperature may even be so low as to lie in the range in which a solid phase occurs, corresponding to the phase diagram applying
110 to the binary system.

- If the temperature of the bath is so high that the liquid two-phase state still prevails, the membrane structures formed have to be rapidly hardened which may be done by correspondingly reducing the temperature after a certain distance in the bath.
120

- It is important that the extruded mixture should still comprise a single phase before entering the bath, i.e. there should still be no
125 significant separation into two phases.

- It has proved to be advantageous, particularly when the membrane is to be produced in the form of a tubular film or hollow filament, for the bath to be preceded in certain cases by
130 a spinning tube which is also filled with the

bath liquid and which dips into the spinning bath. The spinning tube may comprise a conventional spinning funnel at its inlet end and may be curved at its lower end in order to make it easier to draw the membrane through the bath.

The spinning tube may be filled through a level vessel which surrounds and overflows into the spinning tube. In order completely to fill and maintain the level in the spinning tube, more bath liquid has to be delivered to this level vessel from a main reservoir than flows off through the spinning tube. The excess bath liquid may be returned to the main reservoir through a second overflow on the level vessel. The main reservoir and the level vessel may be thermostatically controlled.

On leaving the spinning bath, the membrane may be washed out with a suitable extractant. A number of solvents, such as acetone, cyclohexane and ethanol, also mixtures thereof, may be used for extraction.

In some cases, there is no need for the membrane to be washed out, particularly when the inert liquid used is itself intended to impart certain additional properties to the filament for its subsequent application or is itself intended to perform a function. Thus, it is possible, for example, to use liquids which have an antistatic effect or which act as lubricants.

For numerous applications, it has proved to be advisable to maintain an air gap between the exit surface of the extrusion die, i.e. the exit surface of, for example, a corresponding nozzle, and the surface of the bath. By varying the air gap, it is possible to influence the structure of the membrane obtained and, in particular, its surface.

It has been found that the number of open pores in the surface may be reduced by lengthening the air gap and increased by shortening the air gap. The diameter of the pores also decreases with an increasing air gap.

The air gap may be heated, for example to a temperature above the dissociation temperature of the extruded mixture.

In general, the air gap is at least approximately 1 mm wide and, depending on the working conditions, may assume a length of up to approximately 10 cm. It is important that no separation or at least no significant separation into two liquid phases should occur in the air gap before entry into the bath. As mentioned above, this may be controlled by the shortness of the distance or by heating, although it is also possible to counteract premature separation by increasing the exit speed from the nozzle.

In one particular embodiment of the present process, however, the homogeneous mixture is directly extruded into the bath, open pores having a maximum diameter being formed on the surface.

The membranes obtained may be effectively used as filters. They may be used above all for microfiltration and ultrafiltration. The membranes are particularly suitable for use in the medical field where they may be employed, for example by virtue of the selectivity thereof, for the separation of bacteria and in the filtration of blood, for example for the separation of blood platelets. They are also very suitable for use as oxygenators where oxygen flows through the interior of the membrane whilst blood circulates around its exterior.

For numerous applications, the membranes may also be used as a membrane supports for other membrane layers. By virtue of the outstanding smooth surface structure having open pores, they may be coated extremely effectively with a firmly adhering thin layer of a material acting as membrane, which in many cases is done by coating or spraying with corresponding film-forming solutions. By virtue of the outstanding surface properties thereof, the membrane layer formed adheres very firmly to the present membranes. The coating solution may be applied very uniformly in the form of a thin skin without the solution penetrating or even entering dropwise into the interior of the hollow filament, so that extremely effective membrane combinations for a variety of different applications may be produced in this way.

By virtue of the particular surface structure and the internal structure thereof, the membranes are also eminently suitable for use as substrates for certain substances. It is also possible to introduce the active substance into the continuous hollow interior of a hollow-filament membrane.

It is possible in this way to obtain structures in the form of flat films, tubular films or hollow filaments or sections thereof which slowly release the active substance taken up. The present membranes may also be used for the adsorption of substances.

According to the present invention, it is possible to obtain hollow films of standard dimensions, for example having a thickness of from 20 microns to a few millimetres. The films may be either flat films or tubular films.

The films may also be used as insulating material, for example for heat and sound insulation.

According to the present invention, it is possible to obtain hollow filaments having a wide range of diameters. Thus, it is possible to obtain external diameters of up to several millimetres. The wall thicknesses are also variable within wide limits and may amount, for example, to between 20 microns and about 1 to 2 millimetres.

The pores in the present membranes may have a variety of different shapes. Thus, they may be spherical or elongate and communicate with one another partly through small connecting cavities and partly by merging

directly into one another. Even in the case of membranes which have been obtained from mixtures containing only about 30% of polymer, the polymer may still be the matrix in which the individual pores are distributed and form more or less discrete, but inter-connected cavities. Conversely, it is also possible to obtain structures in which, much the same as in non-woven structures, the cavities form the matrix and the polymer substances is present in a substantially fibril-like arrangement. The boundaries between these two structures are fluid, and, in some cases, occur in mixed form. The structural forms may also be influenced by other process parameters, such as the take-off rate, the cooling rate and deformation within the nozzle.

The present membranes according to the invention are also distinguished above all by the high permeability thereof to gases, such as nitrogen or air. The permeability of the membranes may be expressed by the so-called permeability coefficient K , as discussed in detail in R.E. Collin's book entitled "Flow of Fluids Through Porous Materials", Reinhold Publishing Corp., New York, 1961, page 10, where K is defined as:

$$K = \frac{Q \cdot \eta}{A (\Delta P / h)}$$

wherein Q represents the volume flow per unit of time (for example m^3/s); η represents the viscosity of the following medium ($\text{Pa} \cdot \text{s}$); A represents the mean surface through which the gas emerges; ΔP represents the pressure difference (Pa); and h represents the wall thickness.

The permeability coefficient of the present membranes amounts at least $10 \times 10^{-12} \text{cm}^2$, preferably at least $22 \times 10^{-12} \text{cm}^2$, although values in excess of $100 \times 10^{-12} \text{cm}^2$ may be reached.

In the case of membranes in the form of flat films or tubular films, the coefficient was measured using nitrogen applied under pressure to a film held in a flange. The air issuing through the films is measured by means of a flow meter.

In the case of films according to the present invention produced from a mixture of 30% by weight, of polypropylene and 70%, by weight, of N, N -bis-(2-hydroxy ethyl)-hexadecyl amine with an air gap maintained between the nozzle and the bath, the following values were measured:

	K (10^{-12}cm^2)	Air gap (mm)
60	52	5
	27	10

In the case of hollow filament membranes, measurement was carried out as follows:

31 cm long hollow filaments are embedded

in two 5 cm long flexible PVC tubes by means of a hardenable polyurethane composition.

After the polyurethane was hardened, one of the PVC tubes is cut and the exposed openings are connected through a pipe to a nitrogen bottle, the end of the other flexible tube being tightly closed with a stopper. The air issuing through the filaments is measured by means of a flow meter.

In the case of membrane hollow filaments according to the present invention produced from a mixture of 30%, by weight, of polypropylene and 70%, by weight, of N, N -bis-(2-hydroxy ethyl)-hexadecyl amine with an air gap maintained between the nozzle and the bath, the following values were measured:

K (10^{-12}cm^2)	Air gap (mm)
99	3
85 22	20

The membrane hollow filaments according to the present invention may also be used as an insulating material.

One suitable apparatus for producing the membrane hollow filaments according to the present invention is illustrated in the accompanying drawing. The reference 1 denotes a thermostatically controllable container from

which the inert liquid is metered into the mixer 8 by a double-piston pump 3 and another heater 4. The heater 2 is used for preheating. From the chip container 5, polypropylene passes via an extruder 6 and a gear pump 7 into the mixer 8 from which a hollow filament nozzle 10 is fed via a gear pump 9, being supplied with the necessary quantity of nitrogen via a rotameter 17. The issuing mass passes via an air gap into a spinning tube 12 which is provided with a spinning funnel 11 and which is supplied with an inert liquid from the main reservoir 14 via a level vessel 13. The spinning tube is curved at its lower end. After leaving the bath 15, the filaments are wound up at 16.

The present invention is illustrated by the following Examples:

EXAMPLE 1

Polypropylene having a melt index of 1.5g/10 mins. is melted in an extruder at heating temperatures of from 260 to 280°C and the resulting melt is metered via a gear pump into a highly effective pinned-disc mixer.

At the same time, N, N -bis-(2-hydroxy ethyl)-hexadecyl amine is metered into the mixer through a separate pipe by means of a double piston pump after having been preheated to 135°C in a straight-flow heater.

The mixing ratio of polypropylene to amine is 30:70. The rotational speed of the mixer is adjusted to 400 revolutions per minute.

After passing through the mixer, the two homogenised substances are delivered under

pressure by means of a gear pump to a hollow filament nozzle (internal diameter 2000 μm , free annular gap 400 μm) at a rate of 15 g per minute. Formation of the hollow filament is obtained by the introduction of 4 l/h of nitrogen into the gas capillary of the nozzle.

After a free fall of 3mm, the issuing molten filament enters the spinning funnel filled with amine as the precipitant, flows with the precipitant through the adjoining spinning tube (diameter 8 mm, length 400 mm) and, after passing through an adjoining spinning bath 1 metre long, is wound up at a speed of 7 metres per minute by means of a winding unit.

The hollow filament obtained is extracted with alcohol and freed from the amine.

The hollow filament has a diameter of 2200 μm and a lumen of 1400 μm .

EXAMPLE 2

Polypropylene chips are melted in an extruder and metered via a gear pump into a pinned-disc mixer.

At the same time, liquid N,N-bis-(2-hydroxyethyl)-hexadecyl amine having a temperature of 40°C is pumped from a heatable storage vessel into an electrically heated heater via a double piston pump, passing from the heater into the mixer at a temperature of approximately 150°C. A pinned-disc mixer is used as the mixer.

After the two components have been homogenised, the melt is forced by a measuring pump through a slot die and extruded into a bath which consists of pure N,N-bis-(2-hydroxyethyl)-hexadecyl amine and which has a temperature of 50°C. After the flat film has passed through the bath, which has a length of 50 cm, the film obtained is extracted with ethanol and dried. A film having excellent membrane properties and a particularly good surface structure is obtained.

CLAIMS

1. A membrane in the form of a flat film, tubular film or hollow filament of synthetic polymers which has from 10 to 90%, by volume, of inter-communicating pores and a smooth surface comprising open pores, the proportion of openings in the surface amounting to from 10 to 90%.

2. A membrane as claimed in claim 1, having an apparent density of from 10 to 90% of the true density of the polymer used.

3. A membrane as claimed in claim 1 or claim 2, having a permeability coefficient of at least $10 \times 10^{-12} \text{cm}^2$.

4. A membrane as claimed in claim 1 substantially as herein described.

5. A membrane as claimed in claim 1 substantially as herein described with reference to the Examples.

6. A process for the production of a mem-

brane as claimed in claim 1 which comprises extruding a homogeneous mixture of at least two components, one component being a fusible polymer and another component being a liquid inert to the polymer and both components forming a binary system which, in liquid aggregate state, has a region of complete miscibility and a region with miscibility gaps, at a temperature above the dissociation temperature into a bath which contains the inert liquid of the extruded component mixture and which has a temperature and hardening the membrane formed in the form of a flat film, tubular film or hollow filament.

7. A process as claimed in claim 6, in which the membrane is washed with a solvent after hardening.

8. A process as claimed in claim 7, in which acetone is used for washing.

9. A process as claimed in any of claims 6 to 8 in which an air gap is maintained between the exit surface of the extrusion die and the surface of the bath.

10. A process as claimed in claim 9 in which the air gap is heated.

11. A process as claimed in any of claims 6 to 8 in which the homogeneous mixture is directly extruded into the bath.

12. A process as claimed in any of claims 6 to 11 in which the temperature of the bath is at least 100°C below the dissociation temperature of the binary mixture used.

13. A process as claimed in any of claims 6 to 12 in which the homogeneous mixture is initially extruded into a spinning tube preceding the bath and filled with the bath liquid.

14. A process as claimed in any of claims 6 to 13 in which polypropylene is used as the polymer.

15. A process as claimed in any of claims 6 to 14 in which N,N-bis-(2-hydroxyethyl)-hexadecyl amine is used as the inert liquid.

16. A process as claimed in any of claims 6 to 15 in which a temperature-graduated bath is used.

17. A process as claimed in any of claims 6 to 16 in which a homogeneous mixture of from 10 to 90%, by weight, of polymer and from 90 to 10%, by weight, of inert liquid is used.

18. A process as claimed in any of claims 6 to 17 in which the two components are continuously mixed before extrusion.

19. A process as claimed in claim 18 in which a pinned-disc mixer is used for mixing.

20. A process as claimed in claim 6 substantially as herein described.

21. A process as claimed in claim 6 substantially as herein described with reference to the Examples and/or the accompanying drawing.

22. A membrane as claimed in claim 1 when produced by a process as claimed in any of claims 6 to 21.

23. The use of a membrane as claimed in

any of claims 1 to 5 or 22 as a filter.

24. The use of a membrane as claimed in any of claims 1 to 5 or 22 as a microfiltration filter.

5 25. The use of a membrane as claimed in any of claims 1 to 5 or 22 as a membrane support.

26. The use of a membrane as claimed in any of claims 1 to 5 or 22 as a supporting

10 substrate.

27. The use of a membrane as claimed in any of claims 1 to 5 or 22 as an oxygenator.

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